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14. ABSTRACT The overall objective of this project is to rationally design and create organic materials with high nonlinear refractive index and low single- and two-photon absorption at wavelengths relevant to optical communications. Such materials would open up new capabilities in all-optical switching. Our approach to achieving this objective is to design and synthesize molecules with a twisted zwitterionic-ground-state structure that provides a multitude of low-lying closely-spaced excited states. These are coupled with different donor and acceptor groups and known 3rd-order active molecules to optimize real 3rd-order NLO response at wavelengths of interest. Coupling to the high density of states of ultrasmall metal nanoparticles and use of plasmonic field enhancement from anisotropic plasmonic nanostructures provide routes to further enhancement of the 3rd-order NLO response in these molecules. Head-to-tail aggregation of these molecules can also enhance 3rd-order NLO response through microscopic cascading of 2nd-order nonlinearity. Chiral control of nonlinearity has also been studied.					
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Abstract: The objective of this project was to reveal and implement design principles that maximize the real component of the third-order NLO coefficient, while minimizing the imaginary component, with target figures of merit: $W \equiv n_2 I / (a_1 \lambda) \gg 1$ and $T \equiv a_2 \lambda / n_2 \ll 1$, in a single material. A key feature of this effort was the use of new design principles that are radically different from conventional approaches such as extending chromophore planar π -system, adjusting bond length alternation and inducing intramolecular charge transfer. Our alternate strategies for producing very large γ chromophores focused on (i) twisted π -electron chromophore systems, (ii) microscopically cascaded systems, and (iii) chiral chromophore structures. Guided by multiscale modeling incorporating Time-Dependent Density-Functional Theory (TDDFT) response theory to predict both the real and imaginary parts of γ and, thus, T and W , we designed and synthesized several high-response twisted chromophores with zwitterionic-ground-state structures that provide a multitude of low-lying closely-spaced excited states to produce large $\chi^{(3)}$. We also introduced another design strategy in which we synergistically coupled enhancement due to rich density of states in twisted chromophore with the enhancement due to favorable bond alternation in a cyanine dye. We designed, synthesized and experimentally demonstrated this synergistic effect producing very large $\chi^{(3)}$, substantially exceeding the sum of the two contributions. We also studied the newly proposed microscopic cascading mechanism, where twisted chromophores with large 2nd-order microscopic nonlinearities in computationally-optimized geometries can derive large 3rd-order nonlinearities, without introducing new loss mechanisms. Using multiscale modeling, we designed, synthesized and characterized several highly chiral conjugated polymers that exhibited unprecedented values of chiral nonlinearity. Multiscale modeling played a vital role in design of all these structures and contributed toward building a deep understanding of structure-property relations. Joint papers with researchers at AFRL in Dayton have been published, thus aiding in transitioning of our concepts to AFRL.

Twist motif chromophores:

We have demonstrated a new design strategy to pursue large cubic hyperpolarizability, γ , responses in small π -conjugated structures by using steric hindrance to induce chromophore backbone twisting. To understand the structure-property relationships and improve NLO performance over telecommunication wavelengths, we utilized extending the conjugation through both the pyridinium cation motif and the negatively-charged dicyano(phenyl)methanide. We investigated the effect of cross-conjugation and partially delocalized charge on molecular NLO response. A series of donor-acceptor chromophores were designed to study the effect of changing the electron distribution around a twisted molecule with an electron-rich heteroaryl ring. The parent molecule of this series has a pyridinium acceptor core, and a dicyanomethanide donor unit, as in the TMC chromophores, but modified with an electron-rich 3-hexylthiophene bridge. This molecule, $\text{PMe}_3\text{-TC}_6\text{-(CN)}_2$, synthesized in five steps, has a twisted zwitterionic structure based on NMR and optical absorption spectroscopy. Its charge-transfer peak shows a pronounced negative solvatochromism despite the lower calculated twist angle vs. TMC-2, indicating a large difference in ground- and excited- state dipole moments. It is red-shifted by 0.37 eV in methanol vs. TMC-2, indicating a lower transition energy. Both of these observed properties are desirable for enhancing γ , and Z-scan measurements yielded promising n_2 values. To understand its response mechanism, a planar zwitterionic structural analog, P-T-(CN)₂, was synthesized. It showed much lower negative solvatochromism, and a much higher extinction coefficient, indicating better donor-acceptor conjugation, and therefore reduced charge separation. Thus, we proved that the sterically-induced twist in $\text{PMe}_3\text{-TC}_6\text{-(CN)}_2$ is important to

obtain the large charge separation in the ground state. The pyridinium acceptor core was further electronically modified with one or two annelated benzene rings using quinolinium (Q-TC₆-(CN)₂) and acridinium (A-TC₆-(CN)₂) cores. Q-TC₆-(CN)₂ is predominantly zwitterionic in the ground-state, but has a much lower negative solvatochromism, and a high extinction coefficient for the charge-transfer peak. This indicates better donor-acceptor conjugation, which leads to lower charge separation, and may be due to a much lower twist angle, as per our calculations, or stabilization of the neutral quinoidal resonance contributor by the annelated benzene ring.

Coupling of Twisted Chromophores with Cyanines

To further understand the structure-property relationships and improve NLO performance at telecommunication wavelengths, we incorporated a twist motif into third-order optically-active polymethine dyes for synergistic combination of zwitterionic high density of states with bond length alternation (BLA) of the polymethine dye.

Attaching the twisted moiety to an anionic bisdioxaborine terminated cyanine was ineffective due to the electron-richness of the central carbon atom, while in case of three cationic cyanines as substrates, new supermolecular structures were achieved. Cyanine-like absorption spectra with absorption peaks that were red-shifted relative to the parent cyanine precursor were observed for two indolium-terminated polymethine dyes with the twisted chromophore attached. Dramatically negative solvatochromic shifts, about 250 nm from acetonitrile to dichloromethane, were observed for Cy3, a bis(thiopyrylium)polymethine dye, upon incorporation of a twisted chromophore motif (Cy-TICT). Theoretical calculations and z-scan measurements indicated large values of the real and imaginary parts of γ , offering great potential for a plethora of nonlinear optical applications, such as all-optical switching and optical power limiting, exceeding that of both the parent cyanine dye and our previously-reported twist motif chromophore, TMC-2. This large, sign-tunable third-order nonlinear optical (NLO) response was achieved via cooperative coupling of cyanine dye bond-length alternation effects with the rich density of states in zwitterionic twisted π -system. To analyze coupling between zwitterionic and cyanine states, we computed molecular orbitals for the parent and hybrid systems (Fig. 1). We showed that Cy-TICT is clearly a hybrid of the parent chromophore orbital compositions, with multiple transitions (cross-couplings) between the frontier orbitals of parent molecules. Such cross-couplings resulted in strong transition dipole moments between states and thus, in cooperative enhancement of the Cy-TICT nonlinear response. Orbital hybridization also resulted in spectral shifts of the resonances, so there is an exciting opportunity here to manipulate the sign of n_2 at selected wavelengths.

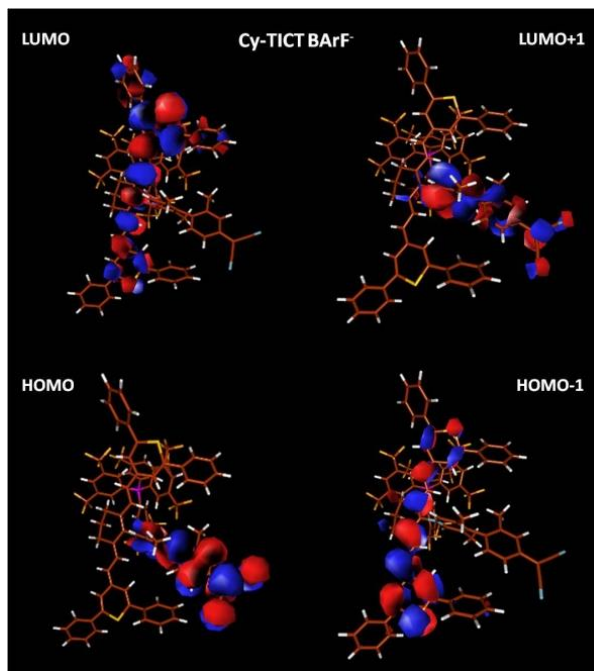


Figure 1. **Cy-TICT** frontier molecular orbitals computed at the DFT CAM-B3LYP/6-31G(d,p) level.

Microscopically cascaded systems:

We developed a phenomenological model for microscopic cascading and showed that the concept of local microscopic cascading of a second-order nonlinearity can lead to a third-order nonlinearity without introducing any new loss mechanisms that could limit the usefulness of our approach. This approach provides a new molecular design protocol, in which the current great successes achieved in producing molecules with extremely large second-order nonlinearity can be used in a supra molecular organization in a preferred orientation to generate very large third-order response magnitudes. The results of density functional calculations for a well-known second-order molecule, (para)nitroaniline, showed that a head-to-tail dimer configuration exhibits enhanced third-order nonlinearity, in agreement with the phenomenological model which suggests that such an arrangement will produce cascading due to local field effects.

New chromophore structures with large chiral nonlinearity:

For the first time we demonstrated that our previously reported PFBT/QD nanocomposites have an exceptionally large value of the effective nonlinear refractive index for right-circularly polarized light, $2.4 \times 10^{-3} \text{ cm}^2/\text{GW}$. This value is more than one order of magnitude larger than that of very promising twisted π -system chromophore TMC-2 that we characterized earlier. For the left-circularly polarized wave the value of the effective nonlinear refractive index was measured to be less than $0.6 \times 10^{-3} \text{ cm}^2/\text{GW}$. Therefore, the value of the nonlinear chirality parameter can be roughly estimated as $0.9 \times 10^{-3} \text{ cm}^2/\text{GW}$ which is comparable with the value of the nonlinear refractive index itself. This provides strong evidence of the enhanced magnetic coupling in the nanocomposite and opens the door to chiral control of optical nonlinearities.

We have also measured the intensity-dependent circular dichroism and circular birefringence of chiral polyfluorene thick film samples using a polarimetric z-scan technique. The intensity dependent refractive index is found to be more than two orders of magnitude larger than that of the quartz plate standard for both senses of the circular polarization. At the same time, the nonlinear chirality parameter is estimated to be of the same order of magnitude as the nonlinear refractive index itself, which makes these chiral polyfluorene films highly suitable for realizing chiral control of optical nonlinearities for a wide range of applications, such as all-optical switching..

We have also synthesized a series of chiral alternating polymers, based on a fluorene-quinoxaline motif with chiral ester side chains (Fig. 2) with much higher optical activity as pure films than the poly(fluorenebenzothiadiazole) (PFBT) that we used in our previous studies. Poly 5 shows a chirality parameter of -0.02 at 360 nm without any doping. The high intrinsic optical activity of these new chiral polymers showed great promise for achieving even higher ultimate

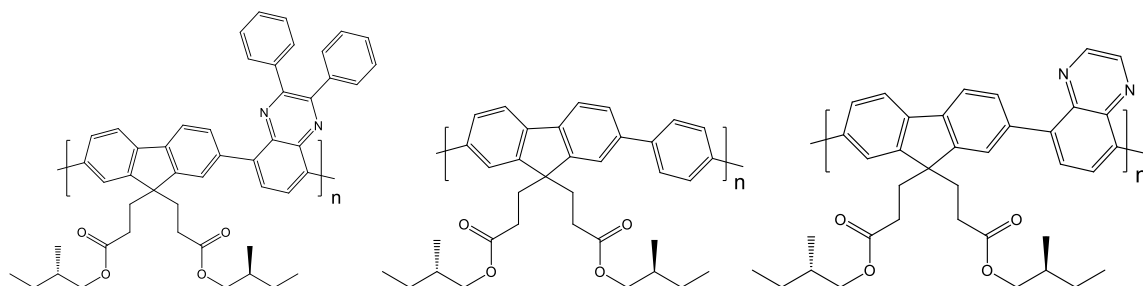


Figure 2. Newly synthesized chiral polymers. From left to right: Poly3, Poly5, Poly 6
Poly 3: poly(9,9-bis(3-((S)-2-methylbutyl)propanoate))fluorene-alt-5,8-(2,3-bis(phenyl)quinoxaline))
Poly 5: (9,9-bis(3-((S)-2-methylbutyl)propanoate))fluorene-alt-1,4-phenyl)
Poly 6: poly(9,9-bis(3-((S)-2-methylbutyl)propanoate))fluorene-alt-5,8-(quinoxaline))

values of chirality parameter, if their interactions with plasmonic nanoparticles and quantum dots, as well as their supramolecular organization, can be optimized. Theoretical calculations revealed a correlation between the topological conformations of oligomers and the simulated CD spectra. Along with the experimental data, this helped clarify the mechanism of optical activity enhancement and provided an insight into strategies for further enhancement of chirality.

Inorganic nanomaterial synthesis

We synthesized ultrasmall gold nanoparticles for coupling with nonlinear dyes and polymers. We have used copper ions to control the growth of two-dimensional gold nanostars with tunable arm length and corresponding tunable localized surface plasmon resonance (LSPR), from five-fold twinned gold nuclei. Ultrathin (<5 nm diameter) gold nanowires have been prepared by a similar approach. These anisotropic structures not only allow tuning of the plasmon resonance position, but also provide dramatic local field enhancement at their vertices (tips). We have produced new semiconductor plasmonic nanocrystals (self-doped copper selenide, copper sulfide, and related materials) with plasmonic resonances tunable from <1000 to >1500 nm wavelength. Combining these approaches, we have grown hybrid structures, in which a self-doped copper selenide domain is grown onto a gold nanoparticle seed to produce dimer particles in which the plasmon resonance of the gold is red-shifted by the presence of the heavily-doped semiconductor, and the resonance of the heavily-doped semiconductor is broadened and blue-shifted by the presence of the gold. This provides a new means of tuning plasmon resonance to wavelengths relevant for optical communications. Linear optical characterization of these structures is complete, and we hope to complete nonlinear characterization of the structures, coupled to the new chromophores described in previous sections, following complete nonlinear characterization of the separate chromophores and nanoparticles.

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